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(54) CARBON MATERIAL FOR ELECTRODE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a carbon material that has a high electrode filling property of material high energy density and a quick charge/discharge property by setting average grain size to be a specific value, surface interval of specific surfaces in a large angle X-ray diffraction method to be shorter than a specific value, specific surface area in a BET method to be less than a specific value, and tap density to have a specific relation with average grain size of the carbon material.

SOLUTION: Average grain size is 2-35 μm , surface interval (d_{002}) of a (002) surface in a large angle X-ray diffraction method is shorter than 0.337 nm, specific surface area in a BET method is less than 18 m^2/g , and tap density is in a range of a formula (TD: tap density of carbon material (g/cm^3) and AP: average grain size of the carbon material (μm)). In argon ion laser Raman spectrum, preferably ratio of peak strength at 1580 cm^{-1} to peak strength at 1360 cm^{-1} is not higher than 0.9, half band width of the peak at 1580 cm^{-1} is not higher than 26 cm^{-1} . After the carbon material for an electrode is mixed with organic compound, the organic compound is carbonized for manufacture.

CLAIMS

[Claim(s)]

[Claim 1] A carbon material for electrodes wherein a spacing (d_{002}) of a field according [mean particle diameter] to 2-35 micrometers and a wide angle X-ray diffraction method (002) is less than 0.337 nm and BET method specific surface area is less than 18 m^2/g and tap density is within the limits expressed with the following (formulas 1).

[Mathematical formula 1]

$1.2 \geq TD \geq 0.0234 \times AP + 0.38$ (formula 1)

(In an upper type TD expresses tap density (unit g/cm³) of a carbon material and AP expresses mean particle diameter (unit μm) of a carbon material)

[Claim 2] A ratio of peak intensity of 1360 cm⁻¹ to peak intensity of 1580 cm⁻¹ in an Ar-ion-laser Raman spectrum or less by 0.9. The carbon material for electrodes according to claim 1 wherein the full width at half maximum of 1580 cm⁻¹ is below 26 cm⁻¹.

[Claim 3] The carbon material for electrodes according to claim 1 or 2 wherein true density is more than 2.21 g/cm³.

[Claim 4] The carbon material for electrodes according to any one of claims 1 to 3 wherein crystallite size is not less than 80 nm.

[Claim 5] The carbon material for electrodes according to any one of claims 1 to 4 wherein mean particle diameter is 30 micrometers or less.

[Claim 6] The carbon material for electrodes according to any one of claims 1 to 5 wherein tap density is more than 0.7 g/cm³.

[Claim 7] A multiple layer structure carbon material for electrodes manufactured by carbonizing this organic compound after mixing the carbon material according to any one of claims 1 to 6 with an organic compound.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the carbon material for electrodes. It is related with the carbon material for electrodes and the multiple layer structure carbon material for electrodes which can constitute in detail the nonaqueous secondary battery which has good quick charge/discharge capability from high capacity.

[0002]

[Description of the Prior Art] In recent years the rechargeable battery of high capacity is needed with the miniaturization of an electronic device. Especially compared with a nickel-cadmium battery and a nickel hydride battery the lithium secondary battery with a high energy density has attracted attention. Although to use a lithium metal at the beginning was tried as the negative pole material while repeating charge and discharge lithium deposited in the shape of resin (the shape of a dendrite) the separator was penetrated even the cathode reached and it became clear that there was a danger of short-circuiting two poles. Therefore attention has been paid to the carbon system material which can avoid generating of a dendrite instead of a metal electrode.

[0003] The cell which adopted the difficulty black lead nature carbon material with a low degree of crystallinity as the negative pole material as a nonaqueous electrolyte secondary battery which uses a carbon system material was marketed first. Then the cell using black lead with a high degree of crystallinity is marketed and it has continued up to now. The electric capacity of black lead is the theory top maximum in 372 mAh/g and if an electrolysis solution is chosen appropriately it can obtain the cell of high charge-and-discharge capacity. Using the carbonaceous material which has the multiple layer structure which is furthermore indicated by JPH4-171677A is also examined. This

combining the strong point (high capacity and irreversible capacity are small) of black lead with high crystallinity (demerit (a propylene carbonate system electrolysis solution is disassembled) and the strong point (it excels in stability with an electrolysis solution) and demerit (irreversible capacity is large) of carbonaceous material with a low degree of crystallinity and employing the mutual strong point efficiently. It is based on the idea of compensating demerit.

[0004] Compared with a difficult black lead nature carbon material crystallinity of black lead (double layer carbonaceous material containing black lead and black lead) is high and its true density is high. Therefore if an anode is constituted using these black lead high electrode restoration nature is obtained and the energy density per volume of a cell can be raised. When it constitutes an anode using the powder of black lead the slurry which mixed the binder with powder and added carrier fluid is created and this is applied to the metallic foil which is a charge collector.

Then the method of drying carrier fluid is generally used.

Under the present circumstances it is common to carry out compression molding further sticking by pressure to a powdered charge collector and for the purpose of equalization of the polar-plate thickness of an electrode and improvement in polar-plate capacity. By this pressing operation the polar-plate density of an anode improves and the energy density per volume of a cell improves further.

[0005] However the particle shape of the available usual high crystallinity graphite material is the shape of a scale, a lepidic form and tabular industrially. When these graphite particles were polar-plate-ized through the above-mentioned polar-plate manufacturing process polar-plate density rose according to the degree of compaction but since a particle gap was not fully secured on the other hand movement of the lithium ion was barred and there was a problem that the quick charge/discharge capability as a cell will fall. When tabular graphite particles are fabricated as an electrode the plate surface of a granular material is arranged by an electrode plate side and parallel with high probability under the influence of the application process of a slurry and the pressing operation of a polar plate. Therefore the edge face of the graphite-crystals which constitutes each granular material particle is fabricated with comparatively high probability by physical relationship vertical to an electrode surface. If charge and discharge are performed in the state of such a polar plate the lithium ion which moves between positive and negative poles and of which black lead inserts and disconnects itself once needs to turn around a powder surface and is remarkably disadvantageous in respect of the move efficiency of the ion in the inside of an electrolysis solution. Since particles were carrying out tabular form the void left behind to the electrode after shaping also had the problem that it will be shut to the electrode exterior. That is since free circulation of an electrolysis solution with the electrode exterior was barred there was a problem that movement of a lithium ion was barred.

[0006] The graphitization thing of spherical meso carbon micro beads is proposed as a negative pole material which on the other hand secures a void required for movement of the lithium ion within a polar plate and it is already commercialized. If the form is spherical even if it passes through an above-mentioned polar-plate pressing operation the spherocity of a crack and an edge face will be maintained for alternative arrangement by each granular material particle and the movement speed of the ion in the inside of an electrode plate will be maintained good. Since the void which furthermore remained

inside the electrode has spherical particle shape and it is in the state connected with the electrode exterior movement of a lithium ion is comparatively free and serves as electrode structure which can respond also to rapid charge and discharge. However since the crystal structure level of meso carbon micro beads as black lead is low the limit of electric capacity is as low as 300 mAh/g and it is already known widely that it is inferior to the shape of a scale and lepidic and tabular black lead.

[0007] Paying attention to these problems invention which specified the form of the black lead used for a nonaqueous electrolyte secondary battery is also performed. JPH8-180873A -- a scale -- invention which specified the ratio etc. of ** particles and the particles which are not scales-like comparatively is indicated. one of these -- JPH8-83610A -- this -- reverse -- more -- a scale -- it is indicated that ** particles are preferred.

[0008]

[Problem to be solved by the invention] The practical use cell is asked for the electrode which combines high electric capacity and the outstanding quick charge/discharge capability. The electrode which fully fills such a demand has not yet come [however] to be provided. For this reason to improve the quick charge/discharge capability of the shape of a scale and a lepidic and tabular graphite material especially is desired strongly. Then it is made for this invention to solve the problem of such conventional technology into SUBJECT. That is it is made to provide the carbon material for electrodes the electrode restoration nature of material is high and is high energy density and which was excellent in quick charge/discharge capability into the issue which should be solved.

[0009]

[Means for solving problem] In order to solve above-mentioned SUBJECT as a result of this invention persons' repeating examination wholeheartedly in order to improve the performance of an electrode it came to acquire knowledge that the outstanding electrode which the form and restoration nature of the graphite material for electrodes are important are carrying out the shape of a ball comparatively and has quick charge/discharge capability and a cycle characteristic with high capacity by using the graphite material or carbonaceous material in which restoration nature has high Electrochemistry Sub-Division capacity highly is obtained.

[0010] The carbon material for electrodes of this invention is completed based on such knowledge. It is characterized by the spacing (d_{002}) of the field according [mean particle diameter] to 2-35 micrometers and a wide angle X-ray diffraction method (002) being less than 0.337 nm and BET method specific surface area's being less than $18 \text{ m}^2/\text{g}$ and tap density being within the limits expressed with the following formulas.

[Mathematical formula 2]

$$1.2 \geq \text{TD} \geq 0.0234 \times \text{AP} + 0.38 \quad (\text{formula 1})$$

(In an upper type TD expresses the tap density (unit g/cm^3) of a carbon material and AP expresses the mean particle diameter (unit μm) of a carbon material)

[0011] The ratio (henceforth a "R value") of the peak intensity of 1360 cm^{-1} to the peak intensity of 1580 cm^{-1} [in / in the carbon material for electrodes of this invention / an Ar-ion-laser Raman spectrum] is 0.9 or less. It is preferred that the full width at half maximum of 1580 cm^{-1} is below 26 cm^{-1} . True density is more than $2.21 \text{ g}/\text{cm}^3$ crystallite size is not less than 80 nm mean particle diameter is 30 micrometers or less and tap density can choose and use especially the carbon material for electrodes that is more than $0.7 \text{ g}/\text{cm}^3$. This invention also provides the multiple layer structure carbon material for

electrodes manufactured by carbonizing this organic compound after mixing these carbon materials for electrodes with an organic compound.

[0012]

[Mode for carrying out the invention] Below the carbon material for electrodes the multiple layer structure carbon material for electrodes and electrode of this invention are explained in detail.

[0013] The carbon material for electrodes of carbon material this invention for electrodes is characterized by the spacing (d002) BET method specific surface area and tap density of the field by mean particle diameter and a wide angle X-ray diffraction method (002) being within the limits of predetermined. The mean particle diameter of the carbon material for electrodes of this invention is within the limits of 2-35 micrometers. As for mean particle diameter it is preferred that it is within the limits of 4-30 micrometers it is more preferred that it is within the limits which is 5-27 micrometers and it is still more preferred that it is within the limits which is 7-19 micrometers. The range indicated by "-" in this Description shows the range including the numerical value indicated before and behind "-." The spacing (d002) of the field according [the carbon material for electrodes of this invention] to a wide angle X-ray diffraction method (002) is less than 0.337 nm. The BET method specific surface area of the carbon material for electrodes of this invention is less than 18 m²/g. As for BET method specific surface area it is preferred that it is below 15 m²/g and it is more preferred that it is below 13 m²/g.

[0014] The tap density of the carbon material for electrodes of this invention is within the limits expressed above (formula 1). "Tap density" as used herein means the bulk density after carrying out 1000 times tapping and it is expressed with the following formulas.

[Mathematical formula 3]

Although the packing structure of the filling body loaded powder object particles of the mass/granular material of a tap density = restoration granular material is influenced by the grade of the size of particles and interparticle interaction power etc. on these Description tap density is being used for it as an index which argues about packing structure quantitatively.

[0015] Although various formulas as a thing showing a tap restoration action are proposed the following (ceremonies 2) can be held as the example.

[Mathematical formula 4]

$\rho_n = A \cdot \exp(-k \cdot n)$ (formula 2)

Bulk density [ρ / ρ_n / the end of restoration] and ρ_n are [here] the bulk density at the time of n times restoration and k and A are constants. "The tap density of the bottom" in this Description refers to a thing wholly as bulk density [of the end by the bulk density at the time of the 1000 times-tapping restoration to a 20 cm³ cell (ρ_{1000})] ρ .

[0016] As long as the carbon material for electrodes of this invention fulfills these conditions other physical properties in particular are not restricted. However the desirable range of other physical properties is as follows. 0.9 or less are preferred for the R value in an Ar-ion-laser Raman spectrum 0.7 or less are more preferred and 0.5 or less are the most preferred. Below 26 cm⁻¹ is preferred for the full width at half maximum of 1580 cm⁻¹ in an Ar-ion-laser Raman spectrum and below its 25 cm⁻¹ is more preferred. As for the true density of the carbon material for electrodes of this invention it is preferred that it is more than 2.21 g/cm³; it is more preferred that it is more than 2.23 g/cm³ and it is still more preferred that it is more than 2.25 g/cm³.

[0017]Even if it uses the carbon material produced naturally the carbon material manufactured artificially may be used for the carbon material for electrodes of this invention. The manufacturing method in particular of the carbon material for electrodes of this invention is not restricted either. Therefore the carbon material for electrodes which has the above-mentioned characteristic for example using judgment means such as sieving and pneumatic elutriation can also be sorted out and acquired. The most desirable manufacturing method is a method of adding and reforming dynamic energy processing to the carbon material produced naturally or the carbon material manufactured artificially and manufacturing the carbon material for electrodes. Then this mechanical energy processing is explained below.

[0018]The carbon materials used as the object which adds mechanical energy processing are natural or artificial graphite powder and carbonaceous powder which is black lead precursors. Such graphite powder and carbonaceous powder have that preferred whose true density less than 0.340 g/cm³ and crystallite size (Lc) are not less than 30 nm and a spacing (d002) is more than 2.25 g/cm³. That whose spacing (d002) is less than 0.338 nm especially is more preferred and what is less than 0.337 nm is still more preferred. As for crystallite size (Lc) what is not less than 80 nm is more preferred and what is not less than 100 nm is still more preferred. As for mean particle diameter what is not less than 10 micrometers is preferred what is not less than 15 micrometers is more preferred what is not less than 20 micrometers is still more preferred and what is not less than 25 micrometers is further more preferred. About the maximum of mean particle diameter what is 1 mm or less is preferred what is 500 micrometers or less is more preferred what is 250 micrometers or less is still more preferred and what is 200 micrometers or less is further more preferred.

[0019]Graphite powder and carbonaceous powder can be used as a raw material even if crystallinity is high and it is low. Since the raw material with low crystallinity has comparatively low plane orientation nature and structure has disorder a crushing surface is comparatively isotropic and it is easy to obtain the roundish treating material by performing mechanical energy processing. After performing mechanical energy processing crystallinity can be improved if it heat-treats further.

[0020]In the carbon material used as the object which adds mechanical energy processing black lead for your kind consideration into which the hex-steel side was greatly grown up in plane orientation and the isotropic high-density black lead which gathered isotropically the graphite-grains child-oriented [of your kind consideration] can be mentioned as a high crystallinity carbon material in which the carbon hex-steel plane structure progressed. As black lead for your kind consideration natural graphite from Sri Lanka or a MADAKA scull and the artificial graphite of a high degree of graphitization of what is called kish graphite and a part deposited as carbon of supersaturation from the iron which carried out melting can be illustrated as a suitable thing.

[0021]Natural graphite according to the description Scaly graphite (Flake Graphite) Flaky graphite (Crystalline (Vein) Graphite) it is classified into soil black lead (Amorphous Graphite) ("particulate matter process technology collection" (Industrial technique Center.)) Refer to the clause of black lead of the Showa 49(1974) issue and "HANDBOOK OF CARBON GRAPHITE DIAMOND AND FULLERENES" (Noyes Publications issue). Although flaky graphite of a degree of graphitization is the most expensive at 100% and scaly graphite is expensive at 99.9% after this soil black lead is as

low as 28%. The quality of natural graphite mainly becomes settled by the origin or a vein. Scaly graphite is produced to MadagascarChinaBrazilthe UkraineCanadaetc. and flaky graphite is mainly produced to Sri Lanka. Soil black lead makes the Korean PeninsulaChinaMexicoetc. the main origins. In these natural graphitegenerallyparticle diameter is small and also soil black lead has low purity. On the other handsince there are the strong pointslike a degree of graphitization and impurity quantity are lowscaly graphite and flaky graphite can be preferably used in this invention.

[0022]An artificial graphite can be manufactured by heating petroleum coke or coal pitch coke at 1500-3000 ** under a non-oxidizing atmosphere. In this inventionif for your kind consideration and high Electrochemistry Sub-Division capacity are shown after performing mechanical energy processing and heat treatmentany artificial graphite can be used as a raw material.

[0023]Mechanical energy processing to these carbon materials is performed so that the mean-particle-diameter ratio before and behind processing may become one or less. "The mean-particle-diameter ratio before and behind processing" is the value which ** (ed) with the mean particle diameter before processing the mean particle diameter after processing. Mean particle diameter here is the particle size distribution of the volume reference measured with laser type particle-size-distribution measuring apparatus. If it measures with laser type particle-size-distribution measuring apparatus the particle size distribution which also equalized the particles which have anisotropy in form isotropicand converted them as a ball substantially will be acquired.

[0024]It is made for the mean-particle-diameter ratio before and behind processing to become one or less in the mechanical energy processing which manufactures the carbon material for electrodes of this invention and which is performed for accumulating. On the other handif granulation is carried outa mean-particle-diameter ratio will be one or moreand tap density will also rise. Since returning to the state before processing in the process fabricated eventually is fully expectedthe particulate matter which carried out granulation is not preferred.

[0025]Mechanical energy processing controls particle shape at the same time it reduces grain size so that the mean-particle-diameter ratio before and behind processing of a powder particle may become one or less. In engineering unit operation utilizable for the particle design of grindingclassificationmixinggranulationsurface treatmenta reactionetc.mechanical energy processing belongs to grinding treatment.

[0026]Grinding applies power to a substancedecreases the sizeand refers to adjusting the particle diameter of a substanceparticle size distributionand restoration nature. Grinding treatment is classified according to the kind of power applied to a substanceand processing. The power applied to a substance is divided roughly into fourthe power (impulse force) struck and broken the power (compressive force) to crush the power (grinding power) to mash and the power (shearing force) to shave off. On the other handprocessing is divided roughly into twothe bulk crushing which is made to generate a crack inside particles and is made to spread and the surface grinding cutting off a particle surface. Bulk crushing advances according to impulse forcecompressive forceand shearing forceand surface grinding advances according to grinding power and shearing force. Grinding is the processing which combined variously the kind and processing of the power applied to these substances. The combination can be suitably determined according to a processing purpose.

[0027] Although grinding may be performed using chemical reactions and cubical expansions such as blasting it is common to carry out using mechanical apparatus such as a grinder. As for the grinding treatment used for manufacture of the carbon material for electrodes of this invention it is preferred that it is processing in which the rate that is not concerned with the existence of bulk crushing but a surface treatment occupies eventually becomes high. That is because the surface grinding of particles takes the angle of graphite particles or a carbonaceous particle and introduces a radius of circle into particle shapes so it is important. After bulk crushing progresses to some extent a surface treatment may specifically be performed only a surface treatment may be performed for bulk crushing to ***** and bulk crushing and a surface treatment may be performed further simultaneously. It is preferred to perform grinding treatment which surface grinding progresses eventually and is polished from the surface of particles.

[0028] Equipment which performs mechanical energy processing is chosen from what has possible performing the above-mentioned desirable processing. When this invention persons inquired it became clear that equipment which repeats mechanical works which also included an interaction of particles for impulse force in a subject such as compression, friction and shearing force and is given to particles is effective. When it has the rotor which installed many blades and the rotor specifically carries out a high velocity revolution to an inside of a casing equipment which performs a surface treatment is preferred giving mechanical work such as shock, compression, friction and shearing force to a carbon material introduced into an inside and advancing bulk crushing. It is more preferred by circulating or circulating a carbon material that it is what has a mechanism in which a mechanical work is repeated and given.

[0029] Nara Machine Factory hybridization system can be mentioned as an example of such desirable equipment. When processing using this equipment it is preferred to carry out [second] peripheral velocity of a rotor to rotate in 30-100 m / it is more preferred to carry out [second] in 40-100 m / and it is still more preferred to carry out [second] in 50-100 m /. Although it is also possible to pass a carbon material as for processing it is preferred to make inside of 30-second or more equipment circulate or stagnate and to process it and it is more preferred to make inside of 1-minute or more equipment circulate or stagnate and to process it.

[0030] It is preferred that it performs heat treatment which improves crystallinity further after performing mechanical energy processing when the true density of the carbonaceous powder used as a raw material is not [crystallinity] so high at less than 2.25. It is preferred to perform heat treatment above 2000 °C it is more preferred to carry out above 2500 °C and it is still more preferred to carry out above 2800 °C.

[0031] By performing such mechanical energy processing a radius of circle can be introduced into graphite particles or a carbonaceous particle and the restoration nature of these particles can be improved. Thus it is important so that introducing a radius of circle into particles may explain below. In order to improve the restoration nature of granular material particles it is known from the former that it is good to be filled up with smaller particles so that the void made between particles can be entered. For this reason if grinding etc. are processed to carbonaceous powder or graphite particles and particle diameter is made small it will be thought that restoration nature increases but even if it makes particle diameter small by such a method generally restoration nature will fall on the contrary. This is considered to be because for particle shape to become an infinite

form more by grinding.

[0032]On the other hand the rate that the void of a packed bed occupies falls so that there is much number (coordination number n) of particles in contact with the one particles (view particles) in a granular material particle group. Therefore the size ratio and composition ratio (namely particle size distribution) of particles are important as a factor which affects a filling factor. However the particles of the graphite powder and carbonaceous powder which perform this examination by the spherical particle group like a model and are dealt with by this invention. Even if particle size distribution is controlled by the shape of a scale lepidic form tabular and only general grindinga classification etc. and it tries a filling factor with the method of being higher the high filling state made into the purpose cannot be produced.

[0033]Generally the shape of a scale lepidic and tabular graphite or a carbonaceous particle is in the tendency for restoration nature to get worse so that particle diameter becomes small. This on the surface of; particles which particles infinite-form-size more by grinding "Peel and write" [a "split" and] It thinks for resistance between contiguity particles to become large and to worsen restoration nature by the cause of adhering to more detailed indeterminate form particles by a certain amount of intensity; and also the particle surface in which protuberance form things such as "bending" carry out the increase in generation. These infinite form nature decreases if particle shape approaches a globular form even if particle diameter will become small reduction of restoration nature will decrease and comparable tap density will be shown theoretically also in the end of the diameter carbon powder of the end of large diameter carbon powder or a granule.

[0034]By this invention persons' examination by the carbonaceous or the graphite particles whose true density and mean particle diameter are almost equal it is checked that a value with high tap density is shown so that form is spherical. That is in order to raise tap density it is important to make the form of particles roundish and to bring close to it spherically. If particle shape approaches spherically restoration nature's of a granular material will improve greatly.

[0035]In this invention the tap density of a granular material is adopted as the index of the degree of conglomeration for the above Reason. When the restoration nature of the particulate matter after processing is going up compared with processing before the result in which particles spheroidized with the used disposal method can be considered. The tap density of the carbon material obtained when it processes reducing particle diameter greatly can consider the result of having spheroidized also when high compared with the tap density of the carbon material of the comparable particle diameter obtained by general grinding.

[0036]The multiple layer structure carbon material for electrodes of multiple layer structure carbon material this invention for electrodes can be prepared by baked-carbonizing this organic compound after mixing the organic compound carbonized by the baking process and the carbon material for electrodes of this invention which has said characteristic. If the organic compound mixed with the carbon material for electrodes is carbonized by calcinating the kind in particular will not be restricted. Therefore even if it is an organic compound which advances carbonization by the liquid phase it may be an organic compound which advances carbonization by the solid phase.

[0037]As an organic matter which advances carbonization by the liquid phase for example The coal tar pitch from a soft pitch to a hard pitch Direct-current system heavy oils such as

Carboniferous system heavy oils such as coal liquid and asphaltene crude oil. Heat treatment pitches etc. which are obtained by heat-treating petroleum system heavy oils such as naphtha tar division-into-equal-parts solution system heavy oil which carries out a byproduct at the time of pyrolysis such as naphtha and decomposition system heavy oils such as an ethylene tar pitch. FCC decantation oil and the Ashland pitch can be mentioned. Furthermore, polyvinyl chloride, polyvinyl acetate, polyvinyl butyral, A vinyl system polymer and 3-methyl phenol formaldehyde resin such as polyvinyl alcohol. Sulfur ring compounds such as nitrogen ring compounds such as aromatic hydrocarbons such as substitution phenol resins such as 35-dimethylphenol formaldehyde resins, acenaphthylene, decalene, and anthracene, phenazine, and an acridine and a thiophene etc. can be mentioned.

[0038] As an organic compound which advances carbonization by the solid phase. For example, chain polyvinyl resins such as naturally-occurring polymers such as cellulose, polyvinylidene chloride, and polyacrylonitrile. Thermosetting resins such as aromatic system polymers such as polyphenylene, furfuryl alcohol resin, phenol-formaldehyde resin, and imide resins. Thermosetting resin raw material like furfuryl alcohol etc. can be mentioned.

[0039] The typical manufacturing method which consists of the following processes as a method of manufacturing the multiple layer structure carbon material for electrodes of this invention from these organic compounds and the carbon material for electrodes can be illustrated.

(The 1st process) The process of mixing a solvent using a mixer, a kneading machine, etc. of various marketing the carbon material for electrodes, an organic compound, and if needed, obtaining a mixture.

(The 2nd process) The process of obtaining the intermediate product which heated agitating said mixture by remaining as it is or necessity, and removed the solvent.

(The 3rd process) The process of heating said mixture or an intermediate product at 500-3000 °C under inert gas atmosphere such as nitrogen gas, carbon dioxide, and argon gas or a non-oxidizing atmosphere, and obtaining the quality of carbonized material.

(The 4th process) The process of performing grinding, cracking, classifying, processing, etc. and carrying out granular material processing to said quality of carbonized material.

[0040] When mixing the 1st process, a solvent may be used and it is not necessary to use it. When using a solvent, in particular, the kind and quantity are not restricted. An organic compound can be made to adhere to the surface of the powder particle of the carbon material for electrodes by mixing the carbon material for electrodes with an organic compound in the 1st process. Not less than 400 °C of cooking temperature of the 2nd process is not less than 300 °C, usually not less than 500 °C, more preferably, and although a maximum in particular is not limited, it is usually 1500 °C or less, still more preferably 2500 °C or less, more preferably 2800 °C or less, 3000 °C or less. Although the 2nd process can also be omitted, the 3rd process is performed after usually performing the 2nd process and obtaining an intermediate product.

[0041] In heat-treatment of the 3rd process, heat history temperature conditions are important. Although the lower limit temperature changes a little with the kinds and heat histories of an organic compound, usual [not less than 500 °C of / not less than 700 °C of] is not less than 900 °C, still more preferably, preferably. On the other hand, about upper limit temperature, it can raise to the temperature which does not have the structure order which exceeds the carbonaceous of the above-mentioned carbon material for electrodes or

the crystal structure of graphite particles fundamentally. Therefore 3000 °C or less of temperature [2800 °C or less of / 2500 °C or less of] of heat treatment is usually 1500 °C or less especially preferably still more preferably preferably. A heating rate a cooling rate a heat treating time etc. can be arbitrarily set up according to the purpose. After heat-treating comparatively in a low temperature region temperature up can also be carried out to a predetermined temperature.

[0042] Omitting is also possible although the 4th process is a process of performing grinding cracking classifying processing etc. and carrying out granular material processing if needed. The 4th process can also be performed before the 3rd process and can also be performed in great numbers before and after the 3rd process. A batch process or continuous system may be sufficient as the reaction machine used for these processes.

Kazumoto or two or more sets may be sufficient.

[0043] The carbonaceous material of the organic compound origin in the multiple layer structure carbon material for electrodes of this invention is comparatively (henceforth "coverage") usually preferred 0.1 to 50 weight % and 0.5 to 25 weight % more preferably it adjusts one to 15 weight % so that it may become 2 to 10 weight % still more preferably. The mean particle diameter of a volume reference is preferred 2-70 micrometers and 4-40 micrometers of multiple layer structure carbon materials [5-35 micrometers of] for electrodes of this invention are 7-25 micrometers still more preferably more preferably. The specific surface area measured using the BET adsorption method -- desirable -- 1-10 m²/g -- it is more preferably preferred 1-7 m²/g and that it is within the limits of 1-4 m²/g still more preferably. As for the multiple layer structure carbon material for electrodes of this invention in the diffraction diagram of the Raman-spectrum analysis which used the Ar-ion-laser light of wavelength [of 5145 cm]⁻¹ and the X ray wide angle diffraction which made CuK alpha rays the line source it is preferred not to exceed the degree of crystallinity of the graphite particles used as a core or a carbonaceous particle. [0044] Jan R value -- desirable -- 0.01-1.0 -- more -- desirable -- 0.05 to 0.8 -- it is 0.1-0.7 still more preferably. Although tap density may improve further rather than the core graphite material used by carbon coating it is desirable to control within the limits of 0.7-1.4 g/cm³. The effect that the tap density of the carbon material for electrodes used as a core improves further and the form is further roundish by multiple layer structure-ization may show up.

[0045] An electrode can be manufactured using the carbon material for electrodes of electrode this invention or the multiple layer structure carbon material for electrodes. Especially the multiple layer structure carbon material for electrodes of this invention can be used for manufacture of an electrode very preferably. The manufacturing method in particular is not restricted but can be manufactured in accordance with the method generally used. The method of applying the slurry obtained by adding a binding agent a solvent etc. to the carbon material for electrodes or the multiple layer structure carbon material for electrodes and making it slurry form as a typical method to the substrate of metal charge collector such as copper foil and drying can be mentioned. The pack density of a polar plate can be raised and the amount of electrodes per unit volume can also be made to increase by carrying out the roll press of the carbon material for electrodes or the multiple layer structure carbon material for electrodes as it is or carrying out a consolidation with a compression molding machine etc. It can also fabricate in the form of an electrode with compression molding etc.

[0046] As a binding agent which can be used for electrode manufacture To a solvent stable polyethylene polypropylene polyethylene terephthalate Resin system polymers such as aromatic polyamide and cellulose styrene-butadiene rubber Rubber-like polymers such as polyisoprene rubber butadiene rubber and ethylene-propylene rubber Styrene butadiene styrene block copolymer its hydrogenation thing A styrene ethylene styrene-butadiene-rubber copolymer styrene isoprene styrene block copolymer Thermoplastic-elastomer-like polymers such as the hydrogenation thing syndiotactic 1,2-polybutadiene Elasticity resin-like polymers such as an ethylene-vinyl acetate copolymer propylene-olefin (carbon numbers 2-12) copolymer Polymer Compounds Sub-Division which has the ion conductivity of fluorine system polymers such as polyvinylidene fluoride polytetrafluoroethylene and a polytetrafluoroethylene ethylenic copolymer alkali metal ions especially a lithium ion can be illustrated.

[0047] As a polymer which has ion conductivity Polyether system high molecular compound such as polyethylene oxide and polypropylene oxide The bridging body polymer of a polyether compound polyepichlorohydrin polyphosphazene polysiloxane polyvinyl pyrrolidone polyvinylidene carbonate The system which compounded lithium salt or the alkaline metal salt which makes lithium a subject with high molecular compound such as polyacrylonitrile Or the system which blended with this the organic compound which has high dielectric constant such as propylene carbonate ethylene carbonate and γ -butyrolactone and the organic compound of hypoviscosity such as straight-chain-shape carbonate can be used. The ionic conductivity in such a room temperature of ion-conductive Polymer Compounds Sub-Division of more than 10^{-5} S/cm is more than 10^{-3} S/cm more preferably.

[0048] Various kinds of forms can be taken as mixed form of the carbon material for electrodes or the multiple layer structure carbon material for electrodes and a binding agent. For example the form which both particles mixed the form mixed in the form where a fibrous binding agent becomes entangled with the particles of carbonaceous material the form with which the layer of the binding agent adhered to the particle surface of carbonaceous material etc. can be taken. As for both mixing ratio it is preferred to carry out a binding material to 0.1 to 30 weight % to the carbon material for electrodes or the multiple layer structure carbon material for electrodes and it is more preferred to carry out to 0.5 to 10 weight %. If 30 weight % or more of a binding agent is added the internal resistance of an electrode will become large and at 0.1 or less weight % it is in the tendency which is inferior in a binding property with a charge collector the carbon material for electrodes or the multiple layer structure carbon material for electrodes conversely.

[0049] The electrode which consists of a carbon material for electrodes of this invention or a multiple layer structure carbon material for electrodes The density of the active material layer on the electrode by which consolidation was carried out by performing a roll press compression molding etc. $0.5\text{--}1.6\text{ g/cm}^3$ The capacity per unit volume of a cell can be pulled out to the maximum without spoiling efficient discharge and the low-temperature characteristic by considering it as $0.7\text{--}1.55\text{ g/cm}^3$ preferably. Since it is close to a globular form at this time that the tap density of the carbon material of this invention is high, i.e. a carbon material it is considered that diffusion of a lithium ion is performed more smoothly few therefore that the void in an electrode is shut.

[0050] Thus a cell which constituted a metal chalcogenide type cathode and a carbonate

system solvent for lithium ion batteries by which use a produced electrode as an anode and normal use is carried out combining organic electrolysis liquid made into a subject. Capacity is large, irreversible capacity accepted in an initial cycle is small, preservability and reliability of a cell in neglect under an elevated temperature are high and it excels in an efficient discharge characteristic and a discharge characteristic in low temperature extremely. About selection of a required component, restrictions are not provided at all on battery constructions such as a cathode and an electrolysis solution.

[0051]

[Working example] An example is given to below and this invention is explained to it still more concretely. Material, the amount used, a rate of operation etc., which are shown in the following examples can be suitably changed unless it deviates from the meaning of this invention. Therefore, the range of this invention is not restricted to an example shown below.

[0052] (Embodiment 1) The black lead 100g was processed using a 1 type (in Table 1 it is called "equipment a") or Turbo Industrial company make T-400 type [made from Nara Machine Factory hybridization system NHS-] turbo mill (4J type) (in Table 1 it is called "the equipment b"). Peripheral velocity and processing time of a kind of graphite material, a kind of processing unit and a rotor were set up as indicated in Table 1 and eight kinds of carbon materials for electrodes were prepared.

[0053] About each prepared carbon material for electrode, the following physical properties were measured respectively.

(1) The 2 volume % solution (about 1 ml) of polyoxyethylene (20) sorbitan monolaurate which is a mean-particle-diameter surface-active agent is mixed to the carbon material for electrodes. The mean particle diameter (median size) of the volume reference was measured by making ion exchange water into carrier fluid with the laser diffraction type particle-size-distribution plan (LA-700 by Horiba Ltd.).

(2) Add about 15% of X ray standard high-purity-silicon powder to the carbon material for X diffraction electrodes and it mixes. The obtained mixture was filled in the sample cell and by making into a line source the CuK alpha rays monochromatized by the graphite monochromator by the reflection type diffractometer method, the wide angle X diffraction curve was measured and it asked for a spacing (d_{002}) and crystallite size (L_c) using Gakushin method.

[0054] (3) After heating at 350 °C for predrying and passing nitrogen gas for 15 minutes using AMS-8000 by BET specific surface area Ohkurariken CO., LTD., it measured by the one BET method by nitrogen gas adsorption.

(4) A tap density granular material density tool (Seishin Enterprise tap DENSA KYT-3000) is used. The screen of 300 micrometers of openings was used as a screen which the carbon material for electrodes penetrates after dropping the granular material in the tap cell of 20 cm³ and filling it up with a cell to the limit 10 mm of stroke length's tap was performed 1000 times and the tap density at that time was measured.

(5) 0.1% of true density surface-active agent solution was used and it measured with the liquid phase substitution method by a pycnometer.

[0055] (6) In the Raman-spectrum analysis using Ar-ion-laser light with a wavelength of 514.5 nm using NR-1800 by the Raman measurement date duty light company, measuring the intensity IA of peak PA near 1580 cm⁻¹ and the intensity IB of the peak PB of the range of 1360 cm⁻¹ -- the ratio of the intensity -- the full width at half maximum near

$R=IB/IA$ and 1580 cm^{-1} was measured. It measured by rotating a cell in a field vertical to a laser beam having filled up the cell with the carbon material for electrodes of powdered voice by the natural fall and irradiating the sample surface in a cell with a laser beam at this time.

[0056] The measurement result of these physical properties is collectively shown in Table 1.

[Table 1]

[0057] The physical properties of the black lead used as a raw material are shown in Table 2.

[Table 2]

[0058] (Embodiment 2) 3 kg of predetermined carbon materials and petroleum system tar which are indicated in Table 3 were milled by supplying 1 kg to M20 type rhe DIGE mixer by Pine Bow company (content volume of 20 l.). Then after carrying out temperature up and carrying out detarring processing to 700 °C under a nitrogen atmosphere it heat-treated by carrying out temperature up to 1300 °C. The obtained thermally treated material was cracked in the pin mill classifying processing was performed in order to remove a coarse particle and four kinds of multiple layer structure carbon materials were prepared eventually. About each multiple layer structure carbon material the R value of coverage, mean particle diameter, a BET specific surface area, a tap density and the Raman measurement was measured. It asked for coverage according to the following formulas and other values were calculated by the same method as Embodiment 1.

[Mathematical formula 5]

(As for the quantity (kg) of a carbon material and T in an upper type the quantity (kg) before detarring processing of kneaded material and N of the quantity (kg) of petroleum system tar and D are [K] the thermally-treated-material recovery amounts (kg) after heat treatment)

[0059] A result is summarized in Table 3 and shown.

[Table 3]

[0060] (Example of an examination) The half cell was produced using the prepared carbon material and the charging and discharging characteristic was examined.

1) What added the dimethylacetamide solution of polyvinylidene fluoride (PVdF) to the creation carbon material 5g of the half cell 10 weight % by solid content conversion was agitated and the slurry was obtained. This slurry was applied on copper foil with the doctor blade method and predrying was performed at 80 °C. After carrying out a consolidation with a roll press machine so that polar-plate density may furthermore become 1.4 g/cm^3 or 1.5 g/cm^3 it pierced to discoid 12.5 mm in diameter reduced pressure drying was carried out at 110 °C and it was considered as the electrode. After an

appropriate time after an appropriate time the coin cell which the electrode and the lithium metal electrode were made to counter focusing on the separator which made the electrolysis solution impregnate was created and the charge and discharge test was done. As an electrolysis solution what dissolved lithium perchlorate in the solvent which mixed ethylene carbonate and diethyl carbonate by the ratio of the weight ratio 2:8 at a rate of 1.5 mol/l. was used.

[0061] 2) It charged to 0V by measuring electric-current density 0.16 mA/cm^2 of irreversible capacity and the 1st service capacity ***** value was made into irreversible capacity from the 1st charging capacity at the time of subsequently making it discharge to 1.5V by current density 0.33 mA/cm^2 .

3) The charge to 0V in measuring electric-current density 0.16 mA/cm^2 of service capacity and quick discharge characteristics and discharge to 1.5V in current density 0.33 mA/cm^2 were repeated 3 times and the 3rd service capacity at that time was recorded with "service capacity." Charge to 0V by current density 0.16 mA/cm^2 and for discharge it Next**** current density 2.8 mA/cm^2 Capacity obtained by carrying out to 1.5V by 5.0 mA/cm^2 was made into the quick discharge capacity in each current density 2.8 mA/cm^2 and 5.0 mA/cm^2 and it was considered as the index of quick discharge characteristics.

[0062] These test results are collectively shown in Table 4.

[Table 4]

[0063]

[Effect of the Invention] It has the feature of the cell using the carbon material for electrodes of this invention or the multiple layer structure carbon material for electrodes having large capacity and the irreversible capacity accepted in an initial cycle being small and excelling in the rapid charging and discharging characteristic further. The discharge characteristic [in / highly / for the preservability and reliability of a cell when it is neglected under an elevated temperature / low temperature] is also extremely excellent. Therefore the carbon material for electrodes of this invention and the multiple layer structure carbon material for electrodes can be used effective in manufacture of cells including a lithium cell.